

REMARKS

New Claims 21 - 30 have been added to more fully claim what applicants regard as their invention.

New Claims 21 - 25 depend directly or indirectly from independent Claim 1; new Claims 26 - 31 depend directly or indirectly from independent Claim 13.

Amended Claims 1 and 13 recite that method is a dry plasma process in which the oxygen and a nitrogen-comprising gas are provided at a volumetric ratio of about 2.5 : 1 to about 20 : 1 oxygen : nitrogen-comprising gas. The amendment of Claims 1 and 13 is supported in applicants' originally-filed Specification at Page 4, lines 20 - 26, continuing through Page 5, line 20. Further support is provided at Page 11, lines 18 - 21, and Page 12, lines 7 - 13, of applicants' originally-filed Specification. Page 11, lines 18 - 20, of applicants' Specification states: "When an inductively coupled high density plasma etch reactor is used, the flow rate of oxygen during this step (the post-etch treatment step) is typically within the range of about 50 sccm and about 200 sccm, most preferably, about 100 sccm." Page 12, lines 11 - 13, of applicants' Specification teaches: "When an inductively coupled high density plasma etch reactor is used, the flow rate of the nitrogen is typically within the range of about 10 sccm and about 20 sccm, most preferably, about 15 sccm." This corresponds to a flow rate ratio within the range of about 2.5 : 1 to about 20 : 1 oxygen : nitrogen.

New Claims 21 and 26 (which depend from Claims 2 and 14, respectively) recite that the hydrogen-containing fluorocarbon gas and the nitrogen-comprising gas are provided at a flow rate ratio of about 1.5 : 1 to about 6 : 1 hydrogen-containing fluorocarbon gas : nitrogen-comprising gas. Claims 21 and 26 are supported at Page 11, lines 18 - 20 and 24 - 26, of applicants' originally-filed Specification. Page 11, lines 24 - 26, of applicants' Specification states: "When an inductively coupled high density plasma etch reactor is used, the flow rate of the hydrogen-containing fluorocarbon gas or gases is typically within the range of about 30 sccm



and about 60 sccm.” (The text found at Page 11, lines 18 - 20, of applicants’ specification, which pertains to the flow rate of the nitrogen-comprising gas, is provided above.) This corresponds to a flow rate ratio within the range of about 1.5 : 1 to about 6 : 1 hydrogen-containing fluorocarbon gas : nitrogen-comprising gas.

New Claims 22 and 27 (which depend from Claims 4 and 16, respectively) recite that the fluorocarbon gas and the nitrogen-comprising gas are provided at a flow rate ratio of about 1 : 2 to about 3 : 1. Claims 22 and 27 are supported at Page 11, lines 18 - 20, and Page 12, lines 3 - 5, of applicants’ originally filed specification. Page 12, lines 3 - 5, of applicants’ specification states: “When an inductively coupled high density plasma etch reactor is used, the flow rate of the fluorocarbon gas or gases is within the range of about 10 sccm and about 30 sccm, most preferably, about 20 sccm.” (The text found at Page 11, lines 18 - 20, of applicants’ specification, which pertains to the flow rate of the nitrogen-comprising gas, is provided above.) This corresponds to a flow rate ratio within the range of about 1 : 2 to about 3 : 1 fluorocarbon gas : nitrogen-comprising gas.

New Claims 23 and 28 recite that the dielectric layer comprises an inorganic dielectric material. New Claims 24 and 29 (which depend from Claims 23 and 28, respectively) recite that the inorganic dielectric material is a silicon-based oxide. New Claims 25 and 30 (which depend from Claims 24 and 29, respectively) recite that the silicon-based oxide is selected from the group consisting of silicon dioxide or borophosphosilicate glass (BPSG). Claims 23 - 25 and 28 - 30 are supported at Page 9, lines 14 - 15 of applicants’ originally filed specification.

#### Claim Rejections Under 35 USC § 102

Claims 1 - 6, 9, 11, and 12 are rejected under 35 USC § 102(e) as being anticipated by U.S. Patent No. 6,248,149, to Li et al.



Applicants respectfully contend that their invention as described in Claims 1 - 6, 9, 11, and 12 is not anticipated or made obvious by the Li et al. reference. The Li et al. reference pertains to the etching of low-k dielectric materials which are primarily carbon containing and which contain no silicon, or less than about 4 % silicon. As a result, the composition of the plasma source gas taught in the Li et al. reference includes a fluorocarbon gas, an oxygen-containing gas (such as oxygen), and nitrogen, where the ratio of nitrogen : oxygen in the etchant plasma ranges between 1 : 1 and 3 : 1 (i.e., the ratio of oxygen : nitrogen ranges between about 1 : 3 to 1 : 1). Further, there is no description of any post-etch treatment for removing etch residues which remain after etching the carbon-based low k dielectric materials, since side-wall build-up material is said to be avoided by the etch process conditions. Applicants' disclosure relates to the plasma etching of silicon-containing dielectric layers. The focus of applicants' invention is a post-etch treatment for removal of residues such as side-wall build up, which residues are created in the dielectric etch process. As a result, applicants' amended Claim 1 pertains to a dry plasma post-etch treatment using a plasma generated from a source gas comprising oxygen, a nitrogen-comprising gas, and a reactive gas comprising hydrogen, carbon, and fluorine, where the volumetric ratio of oxygen : nitrogen in the post-etch treatment ranges from about 2.5 : 1 to about 20 : 1.

Applicants' dry plasma post etch treatment employs an etchant plasma having a composition which is clearly outside of the composition of etchants taught and suggested by the Li et al. reference, which teaches away from using such high oxygen concentrations, as discussed below. The difference in the oxygen : nitrogen ratio is dictated by the difference in composition of the materials to be etched (in applicants' case removed from sidewalls of the structure). The present invention is easily distinguishable from the Li et al. reference.

In more detail, the Li et al. reference pertains to a plasma etching process for etching a carbon-based low-k dielectric layer in a multi-layer inter-level dielectric. The low-k dielectric



may be divinyl siloxane-benzocyclobutene (BCB), which contains about 4% silicon, the remainder being carbon, hydrogen, and a little oxygen. The BCB etch uses an etching gas of oxygen, a fluorocarbon, and nitrogen, with no argon. An  $N_2 / O_2$  ratio of between 1 : 1 and 3 : 1 ( $O_2 : N_2$  ratio of 1 : 3 to 1 : 1) produces vertical walls in the BCB. (Abstract)

Li et al. is cited by the Examiner as teaching a method of etching a dual damascene structure, which method entails first etching a contact hole through upper and lower dielectric layers (as well as through the intervening etch stop layer). After having formed the contact hole, a trench is etched into the upper dielectric layer. The Examiner suggests: "During the etching of the trench, the contact hole that has been etched into the lower dielectric is exposed to the plasma conditions of trench etching step. As such the plasma that etches the trench also constitute a post-etch treatment of the contact hole." However, one skilled in the art would have no motivation to use the trench etch method taught by the Li et al. reference to remove sidewall build-up which forms while etching a dielectric layer of the kind described by applicants, since the Li et al. dielectric does not produce side wall build up of the kind applicants seek to remove. As importantly, as previously discussed, the composition of the plasma source gas used for applicants' post-etch treatment is considerably different from that used by Li et al. to etch an organic low-k dielectric material. In particular, the relative oxygen : nitrogen ratio used by applicants is much higher (from about 2.5 times to about 60 times higher) than that taught in the Li et al. reference.

In the instances where hydrogen is present in the etchant plasma, as it is in applicants' post-etch treatment plasma, the Li et al. reference teaches a nitrogen : oxygen flow ratio between 1 : 1 and 3 : 1 (Col. 5, lines 42 - 43 and Abstract.) The Li et al. reference teaches use of a much larger amount of nitrogen with respect to oxygen to avoid undercutting of the carbon-based dielectric layer which is being etched. At Col. 16, lines 39 - 42, Li et al. states: "A high  $O_2 : N_2$  ratio (that is, a high  $O_2$  flow) increases the BCB etch rate to about 360 nm/min but results in



BCB undercut because of excess oxygen.” Thus, the Li et al. reference teaches away from a plasma source gas of the kind used and claimed by applicants.

With respect to new Claims 22 and 28, applicants recite that the hydrogen-containing fluorocarbon gas and the nitrogen-comprising gas are provided at a flow rate ratio of about 1.5 : 1 to about 6 : 1 of hydrogen-containing fluorocarbon gas : nitrogen-comprising gas. New Claims 23 and 29 recite that the fluorocarbon gas to nitrogen-comprising gas flow rate ratio is about 1 : 2 to about 3 : 1. At Col. 5, lines 40 - 41, Li et al. states: “Preferably, the amount of fluorocarbon is substantially less than the oxygen and the nitrogen.” In Table 1, where the Li et al. reference describes the etching of BCB, the flow ratio of a hydrogen-containing fluorocarbon gas relative to the nitrogen gas is about 1 : 15, and in Table 4, the ratio is about 1 : 7.

Because the purpose of the Li et al. invention (etching of a trench in a BCB layer, without undercutting of the BCB layer) is different from the purpose of applicants' invention (removing residues after a silicon-containing dielectric etch process), a different plasma source gas composition is required.

New Claims 24 and 30 recite that the dielectric layer comprises an inorganic dielectric material; new Claims 25 and 31 recite that the inorganic dielectric material is a silicon-based oxide.; and new Claims 26 and 32 recite that the silicon-based oxide is selected from the group consisting of silicon dioxide or borophosphosilicate glass (BPSG).

In light of the above distinctions, applicants respectfully request withdrawal of the rejection of Claims 1 - 6, 9, 11, and 12 under 35 USC § 102(e) as being anticipated by U.S. Patent No. 6,248,149, to Li et al.

Claims 1 - 18 are rejected under 35 USC § 102(a) as being anticipated by U.S. Patent No. 6,082,374, to Huffman et al.



Applicants respectfully contend that the Huffman et al. reference does not anticipate applicants' invention. The method of plasma generation and the conditions under which the plasma is applied to the substrate are considerably different from those of applicants, because the Huffman et al. apparatus is considerably different from applicants' apparatus. The plasma is generated in a sapphire discharge tube and plasma from the tube is "directed toward" the substrate. Figures 33 and 34 illustrate how the Huffman et al. plasma is generated remotely from a chamber in which the substrate is present. In applicants' apparatus, the plasma is generated in the process chamber in which the substrate is contained, directly over the surface of a substrate being treated. The plasma density of the Huffman et al. plasma at the surface of the substrate is not specifically defined. However, based on the apparatus and the plasma generation conditions, one skilled in the art would conclude that the substrate is not contacted with a high density plasma. In applicants' apparatus, the plasma contacting the substrate is a high density plasma. Typically, based on the numbers provided, the pressure in the Huffman et al. sapphire plasma tube ranges from about 0.5 Torr to about 10 Torr, with the examples being in the range of about 1.5 Torr. A microwave excitation electric field is utilized to generate the plasma. In applicants' apparatus, illustrated in Figure 9, RF power is applied to coils to generate a plasma in the processing chamber, where the pressure typically ranges from about 15 mTorr (0.015 Torr) to about 30 mTorr (0.030 Torr).

The Huffman et al. reference teaches, under the "objects" of the invention, that the goal is to remove residual photoresist PR (as described in Col. 1) and other materials from a substrate while maintaining minimum oxide loss, where a plasma is generated in a sapphire plasma tube and the plasma is directed from the tube toward the material to be removed from a substrate. Applicants are frequently etching a dielectric which is an inorganic oxide, and oxide residue must be removed from the substrate surface.



Further, applicants' method as claimed in Claims 7 - 12 and 13 - 18 does not use a single exposure to a given plasma to remove deposits; instead, a series of steps are used, with the combination of steps designed to produce the desired result.

The processing apparatus and conditions are so different, and the process conditions applied to the substrate are so different between those described in the Huffman et al. reference and applicants' disclosure, that it is not possible to predict with any certainty whether the apparatus and method described in the Huffman et al. reference even could succeed in removing the by-product deposits from applicants' dielectric etch process. Further, in view of the distinctions in the method, it is clear that Huffman et al. does not teach or even suggest applicants' method. Certainly there is no anticipation of applicants' method by the Huffman et al. disclosure.

In more detail, the Huffman et al. reference pertains to a method for removing a material from a substrate, where a plasma is generated in and discharged from a device including a sapphire discharge tube. At least one fluorine-containing compound and a forming gas ( $N_2/H_2$ ) are introduced into the plasma. (Abstract) At Col. 5, lines 4 - 10, the Huffman reference states "although the advantages of utilizing oxygen-containing compound(s), fluorine-containing compound(s), and nitrogen-containing compound(s) or gases that include oxygen, fluorine, and nitrogen may have been known, it was not know to utilize this combination of materials in a sapphire plasma tube". All of the claims in the Huffman et al. patent are limited to a method in which the plasma is generated in and discharged from a sapphire tube. Applicants' invention as described and claimed does not include or even suggest the use of a sapphire plasma tube.

At Col. 5, lines 29 - 32, the Huffman et al. reference states: "The flow rate of the at least one oxygen-containing compound preferably generates a pressure in the plasma tube of from about 0.5 torr (500 mTorr) to about 10 torr (10,000 mTorr). More preferably, the pressure in the process chamber is about 1.5 torr (1,500 mTorr)." All of the examples provided are at 1.5 torr



(Col. 7, lines 18 - 19; Col. 7, lines 62 - 64; Col. 8, lines 8 - 9; Col. 8, lines 34 - 35; Col. 12, both tables; Col. 13, both tables; Col. 15, table; Col. 16, table; Col. 17, tables; and Col. 18, table).

There is a general statement at Col. 6, lines 11 - 13, that the pressure maintained in the plasma generating and discharge device may be from about a few millitorr to about 10 torr. However, this statement is not enabling for applicants' invention, which is limited to the use of a high density plasma which is generated in the process chamber which contains the substrate, and is generated directly over the substrate surface to provide a high density plasma directly over the substrate surface. Further, there is no combination of process conditions, including plasma source gas composition, which is described for use at process chamber pressures in the range of a few millitorr. One skilled in the art is likely to follow the Huffman et al. direction at Col. 5, lines 29 - 32, and in the Examples, where the plasma gas compositions are called out, and the recommended pressure in the plasma tube is in the range of 500 mTorr to 10,000 mTorr. Under these conditions, a high density plasma is not obtained when the plasma source gas composition described and claimed by applicants is used.

Applicants' independent Claims 1 and 13 recite a high density plasma as defined in their application, where the plasma exhibits an ionization density of at least  $10^{11} \text{ e}^- / \text{cm}^3$ . On Page 5 of the present Office Action, the Examiner acknowledges that Huffman does not teach using a plasma with an electron density of at least  $10^{11} \text{ e}^- / \text{cm}^3$ . The Examiner further states that "It would have been obvious to one skilled in the art to us [*sic*] a plasma with an electron density of at least  $10^{11}/\text{cm}^3$  [*sic*] because Huffman teaches that any plasma apparatus may be used and it is well known that a high density plasma provided advantages, such as an increase in processing rate (higher throughput) and generally wider process windows [*sic*] which allow for a higher degree of process control." However, applicants maintain that Huffman does not teach that any plasma apparatus may be used. Huffman teaches that the plasma apparatus must include a sapphire tube in which the plasma is generated. There is no suggestion in Huffman et al. that any



particular ionization density is of benefit. To the contrary, Huffman et al. seems to indicate that any pressure can be used, although pressures of 500 mTorr and above are preferred. This indicates that the Huffman et al. method may be carried out independent of plasma ionization density. By contrast, the use of a high density plasma is an important feature of applicants' claimed invention.

In summary, Huffman et al. recommends the use of plasma processing conditions which will not produce a high density plasma; recites the use of a specialized sapphire plasma tube in all embodiment descriptions and claims; and requires removal of the substrate from the processing chamber for a rinse step, which is not even suggested in applicants' disclosure. Huffman et al. is not enabling for and does not even suggest the series of processing steps described and claimed by applicants. Huffman et al. describes a different method, carried out using different equipment and processing conditions, and achieving different results than those achievable using applicants' presently claimed invention.

In light of the above distinctions, applicants respectfully request withdrawal of the rejection of Claims 1 - 18 under 35 USC § 102(e), over Huffman et al.

#### Claim Rejections Under 35 USC § 103

Claims 1 - 4, 6, 9, and 11 are rejected under 35 USC § 103(a) as being unpatentable over U.S. Patent No. 6,194,128, to Tao et al., in view of U.S. Patent No. 6,036,878, to Collins.

Applicants respectfully contend that a combination of the Tao et al. and Collins disclosures does not provide a prima facie case of obviousness for applicants' invention. The Tao et al. reference pertains to methods of etching dual damascene structures which contain both low k dielectric materials and oxide-based dielectric layers. There are a series of 17 steps described relative to and claimed in independent Claims 1 and 17. There are a series of 15 steps in independent Claim 37. The method steps include forming dielectric layers, forming hard mask



layers, forming photoresist layers, and etching various of these layers. Also included is “performing post cleaning of said dual damascene structure”, depositing metal in the dual damascene structure to form an interconnect, and removing excess metal from the surface of the dual damascene structure. The post cleaning is described as using an amino acid dip at a temperature between about 25 and 50 °C, for a time period of about 5 to 10 minutes. Applicants' method is one for dry plasma cleaning residue from a semiconductor surface only, and does not involve use of an amino acid dip or any other wet dip. The Collins reference relates to “Low Density High Frequency Process For A Parallel Plate Electrode Plasma Reactor Having An Inductive Antenna” (Title) As described in the lengthy disclosure and claimed in Claim 1, the method is one in which an intermediate plasma density (less than a high density plasma) can be maintained inside the process chamber without extinguishing the inductive coupling of the RF field. This process chamber is substantially different from the process chamber in which applicants' invention is carried out, and is designed to provide plasma processing of a substrate using a low to intermediate density plasma, whereas applicants' method is carried out using a high density plasma, as claimed. A combination of these two references does not even suggest applicants' invention.

In more detail, the Tao et al. reference pertains to a method of forming dual damascene interconnects in a semiconductor substrate. Tao et al. is cited by the Examiner as etching a dual damascene structure, where an upper trench structure is etched, and then from the bottom of the trench, a contact hole is etched down through an underlying dielectric layer. The Examiner comments: “While the contact hole is being etched through the lower dielectric layer, the plasma that etches the contact hole is also in contact with the surfaces of the previously etched trench and thereby this plasma also functions as a post-etch treatment for the trench”.

Like Li et al., any treatment of Tao's trench surfaces is a side effect of etching a contact hole through the lower dielectric layer. Tao et al. does not teach a post-etch treatment method.



Further, one skilled in the art would have no motivation to use the etch method taught by Tao et al. as a post-etch treatment in applicants' method . As mentioned above, the post-etch cleaning method taught by Tao et al. is an amino acid wet dip process.

Because Tao et al. is trying to accomplish a different purpose (that is, etching of a contact hole in a dielectric layer), Tao needs a different plasma source gas composition than that used by applicants in their claimed post-etch treatment method. At Col. 6, lines 42 - 46, Tao et al. states: "This oxide etch is also performed in an MERIE with gases nitrogen, oxygen,  $\text{CHF}_3$  (or  $\text{CH}_3\text{F}$ ) and CO at respective flow rates between about 40 to 50 standard cubic centimeters per minutes (sccm), 10 to 20 sccm, 5 to 15 sccm and 1 to 10 sccm . . ." This corresponds to an oxygen : nitrogen flow rate ratio within the range of 1 : 2 to 1 : 5  $\text{O}_2$  :  $\text{N}_2$ . By contrast, applicants post-etch treatment method utilizes an  $\text{O}_2$  :  $\text{N}_2$  flow rate ratio of about 2.5 : 1 to about 20 : 1, as recited in the newly amended independent claims.

Collins is cited by the Examiner as teaching that a typical MERIE reactor operates in a density realm of between  $10^{10} \text{ e}^- / \text{cm}^3$  and  $10^{11} \text{ e}^- / \text{cm}^3$ , and with a chamber pressure of between 25 mTorr and 100 mTorr. Applicants are not claiming the use of a plasma density at a particular pressure as a novel and non-obvious invention alone. It is the combination of all of the elements recited in applicants' claims which provides a novel and non-obvious invention which relates to a post-dielectric etch treatment to remove etch residues. Since there is nothing in the Collins reference which even suggests applicants' method; and, since combining the teachings of Tao et al. with Collins will not direct one skilled in the art to applicants' invention, applicants maintain that Claims 1 - 4, 6, 9, and 11 are patentable over the combination of Tao et al. and Collins for the same reasons that Claims 1 - 4, 6, 9, and 11 are patentable over Tao et al.

In light of the above distinctions, applicants respectfully request withdrawal of the rejection of Claims 1 - 4, 6, 9, and 11 under 35 USC § 103(a), over Tao et al., in view of Collins.



Claims 1 - 4, 6, and 9 - 12 are rejected under 35 USC § 103(a) as being unpatentable over U.S. Patent No. 5,849,639, to Molloy et al.

Applicants respectfully contend that the disclosure in the Molloy et al. reference does not render applicants' invention obvious. The Molloy et al. reference describes the use of a plasma generated from a combination of gases to treat an etched semiconductor structure, to remove a photoresist layer, and to alter the composition of the residues present on the etched substrate surface, so that the residues become soluble in water and can be rinsed off using deionized water. (Abstract) All of the cleaning methods described in the Molloy et al. reference require the use of a water rinse to complete the cleaning of the semiconductor surface. Applicants' method does not require a wet surface treatment of any kind. There is no suggestion of applicants' invention in the Molloy et al. disclosure, which teaches away from applicants' totally dry plasma cleaning technique

In detail, the Molloy et al. reference discloses a gas plasma process for removing photoresist, etch residues, and other contaminants involved in etching vias in integrated circuit devices. "The process involves placing the substrate having etched vias or contact holes in a low bias reactor; applying to the substrate surface a mixture of gases at low bias selected from the group consisting of oxygen, nitrogen, fluorine, hydrofluorocarbon and fluorinated methane and amine gases to both remove the photoresist layer and alter the composition of the residues such that the residues are soluble in water; and rinsing the substrate with deionized water." (Abstract) Molloy's process is carried out at process chamber pressures in the range of 0.7 - 1.5 Torr (refer to Col. 5, lines 6 - 27), which indicates to one skilled in the art that the plasma used in Molloy's process is not a high density plasma.

The presently claimed invention utilizes a dry etch plasma only process to remove photoresist and other byproducts remaining after a dielectric etch process. In contrast to Molloy's process, applicants' claimed method utilizes a high density plasma. At Page 12, lines



23 - 24, of applicants' specification, the post-etch treatment is specified to be carried out at a process chamber pressure ranging between about 20 mTorr and 50 mTorr, which allows for the generation and sustenance of a high density plasma within the processing chamber.

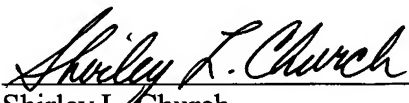
Applicants' claimed method so thoroughly removes the undesirable residues remaining after a dielectric etch that no subsequent water rinse or other wet process is required for the post-etch treated semiconductor structure to be ready for subsequent processing. This is a definite advantage over the teachings of Molloy et al., since the semiconductor structure can be further processed without the need to remove it from the processing chamber for a water rinse.

In summary, Molloy et al. and the subject application describe two different processes, using different operating conditions, and achieving different results.

In light of the above arguments and the amendment to independent Claim 1, applicants respectfully request withdrawal of the rejection of Claims 1 - 4, 6, and 9 - 12 under 35 USC § 103(a), over Molloy et al.

Applicants contend that the presently pending claims are in condition for allowance, and the Examiner is respectfully requested to pass the application to allowance. The Examiner is invited to contact applicants' attorney with any questions or suggestions, at the telephone number provided below.

Respectfully submitted,

  
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